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Latest Progress in Sensors for Pre-explosive Detection of Flammable Gases: A Review

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In this paper, we present a brief review of current trends in the development of technologies for manufacturing sensors of flammable gases and volatile organic compounds at pre-explosive concentrations. Different types of gas sensor, including catalytic, semiconductor, and optical sensors, and the principles of their operation are discussed. The advantages and disadvantages of each type of gas sensor are shown. New and traditional production technologies of sensitive elements are discussed, providing improvements of sensor parameters such as effectiveness, miniaturization, and reduction of energy consumption. In conclusion, we suggest future trends and prospects for research and development to increase the sensitivity and selectivity of sensors.

1. Introduction

There are many industrial plants where explosive gas mixtures can be produced or used as well as a million kilometers of oil and gas pipelines worldwide. Leakage of flammable gases is dangerous and can lead to tragic explosions. Therefore, leakage detection of flammable gases is essential in both industry and daily life.

Even if the warning and prevention of dangerous situations related to the presence of flammable gas mixtures in the atmosphere have already been under development for a long time, many explosion accidents still occur worldwide. The reasons for such accidents include flammable gas leakage and emission during the production, transportation, processing, storage, and use of hydrocarbons. The most frequent reasons for explosions are violations of safety rules during equipment operation, tightness of connections, and the absence of proper control over technological processes. These accidents cause serious property losses and even deaths in both industry and everyday life.

To ensure human safety and continuous control over the environment in industrial and residential areas, there should be a measuring device to identify flammable gases in air. Gas sensors have been considered to be an efficient tool for leakage detection of explosive gases.

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Flammable gases explode only when the gas content in the air is between the lower (LEL) and upper (UEL) explosive limits. LEL and UEL values for widely used chemicals are shown in Table 1.[1] Note that the wider the range between LEL and UEL, the more explosive is the flammable gas.

To control the leakage of flammable gas mixtures, there should be sensors to measure the concentration of corresponding flammable gases in the air in the pre-explosive concentration range, which is usually within 0.1–50% LEL of the corresponding flammable gas or volatile organic compound (VOC).

The studies and the market of gas sensors represent quite well certain sensors and measuring systems designed to monitor gases and gas mixtures at pre-explosive concentrations.[2] In this review, we focus on sensors for the measurement of different hydrocarbons at pre-explosive concentrations, excluding other explosive substances such as ammonium.

In this review, we do not include hydrogen sensors, except for cases when hydrogen is a part of an explosive hydrocarbon mixture (for example, methane, butane, ethanol). This is related to the fact that although hydrogen is classified as an explosive gas, hydrogen sensors are a separate area of research and development. This is largely due to the characteristics of hydrogen: high hydrogen liquidity and explosiveness. Besides, the number of sensors for hydrogen measurement exceeds the number of sensors for hydrocarbon measurement. Hydrogen sensors are described in more detail elsewhere.[3,4]

The most widely used sensors to control pre-explosive concentrations of flammable gases and VOC are metal oxide semiconductor (MOS), catalytic, and optical sensors. Each sensor type has its own benefits and drawbacks. The choice of a sensor for practical use depends on the application field and task.

Although semiconductor, catalytic, and optical sensors have been known for many years, nowadays, studies are being conducted to improve their sensitivity, selectivity, long-term stability and response time. Moreover, the development of wireless sensor networks, autonomous gas detectors, as well as devices for Internet of Things and smart houses faces major challenges, for example, a high energy consumption and measurement methods need to be optimized.[5–8]

Table 1
LEL and UEL of flammable gases and volatile organic compounds (standards: ISO 10156 and EC 60079).

Name of substance	LEL (vol.%)	UEL (vol.%)
Hydrogen H_2	4.0	75
Methane CH_4	4.4	17.0
Ethane C_2H_6	2.5	15.5
Propane C_3H_8	1.7	10.9
Butane C_4H_{10}	1.4	9.3
Pentane C_5H_{12}	1.5	7.8
Hexane C_6H_{14}	1.0	7.5
Acetone C_3H_6O	2.9	13.0
Benzene C_6H_6	1.2	8.6
Kerosene $C_{12}H_{26}$	1.4	7.5
Toluene $C_6H_5–CH_3$	1.1	7.8
Methanol CH_3OH	5.5	36

In this review, we provide a brief analysis of contemporary trends in hydrocarbon sensor development and relevant measurement methods. From among the entire variety of sensor types and measurement methods, we will focus on those trends that have or can have wide practical applications in the nearest future.

2. Semiconductor Sensors

MOS sensor operation is based on changing the conductivity of the sensitive layer when changing the gas environment as a result of its surface gas molecule adsorption.[9] The sensitive layer or element (SE) of gas sensors consists of MOS materials (SnO_2, ZnO, MoO_3, etc.) or organic semiconductors (metalloporphyrins). The most widely used SEs are based on SnO_2, ZnO, MoO_3, and others.[10] Recently, SEs based on indium and gallium oxides have also attracted interest.[11–13]

To conduct measurement, it is necessary to heat the semiconductor layer to a temperature in the range of 200–450 °C. For example, the temperature for maximum gas sensitivity of thin-film sensors based on SnO_2 to ethanol and acetone is 330–400 °C. The same temperature is required for hydrocarbons of homologous methane series. To decrease the temperature for maximum gas sensitivity, the SnO_2 film may be doped with impurities of rare-earth chemical elements or noble metal, but this will complicate the technological process and increase the sensor's cost.[14]

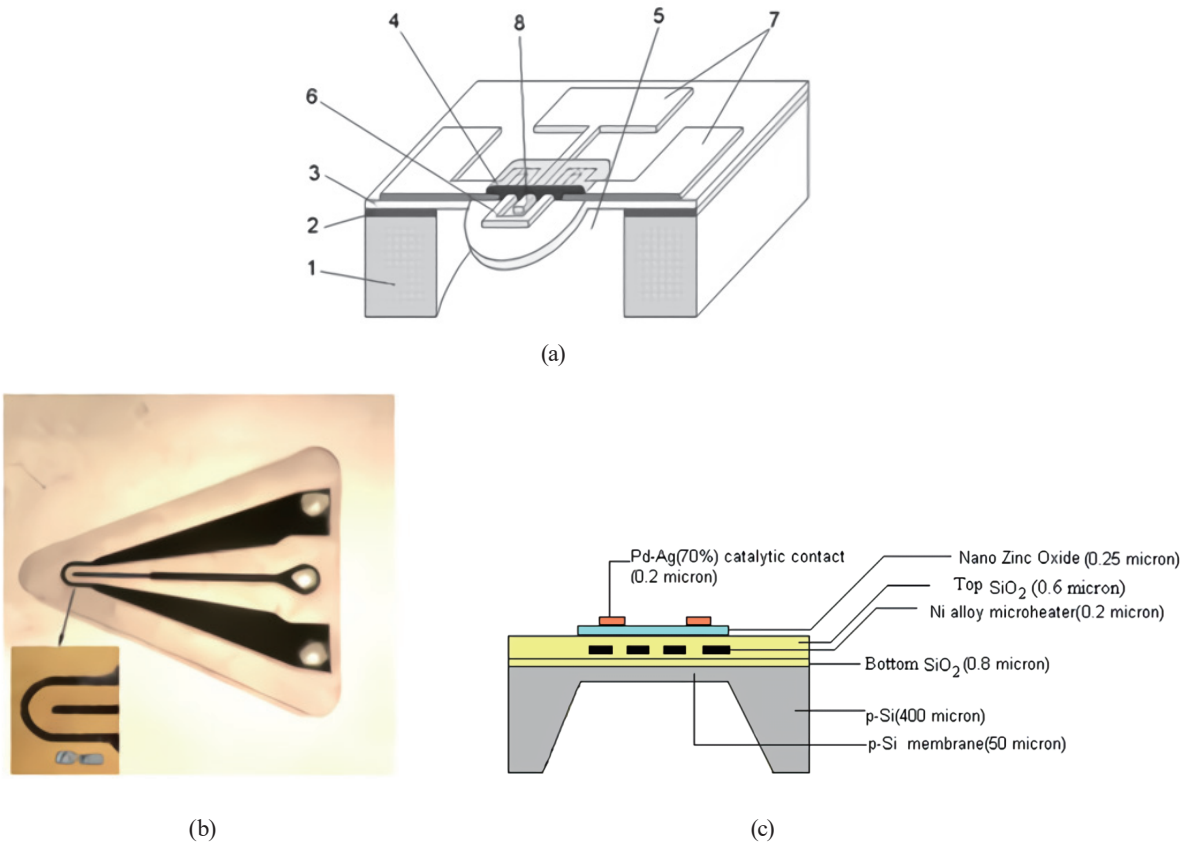
The advantages of semiconductor sensors include high sensitivity, high operation speed, small size, and low cost of mass production. Their main disadvantage is low selectivity, which limits their uses.

Therefore, the main trend in semiconductive sensor development is to increase their selectivity with a simultaneous decrease in their energy consumption, which is required for autonomous gas detectors particularly for wireless sensor networks.[5,15,16]

A typical approach to decreasing the energy consumption of semiconductor and catalytic sensors is to reduce the sensor size in order to reduce the heated volume, including the base layer and heater with a sensitive semiconductor layer on it.[17] To complete the task, the change from volumetric technology to a planar one, where the heater is made to meander on the base layer, is introduced. Platinum, nickel, polysilicon, and nichrome, for example, are used as heater materials. In this case, the base layer should be as thin as possible and, in fact, should be a membrane (Fig. 1).[18]

The structure of the CeraMEMS chip is presented in Fig. 1(a).[19] It consists of a rigid frame made of commercial Rubalit 710TM alumina ceramics (1) with holes; thin alumina film (3) is fixed on this frame with glass binder (2) and covers the laser-drilled hole (5). On top of this film, the sensing layer (4) equipped with the meander-shaped heater (6) and digit electrode (8), was deposited by screen printing or drop deposition techniques. The contact pads to the sensing layer and heater (7) are located in the room-temperature area.

A single chip of the cantilever micro-hotplate after laser processing is presented in Fig. 1(b).[20] The substrates were 30-μm-thick boron-silicate glass with transformation temperature T_g = 720 °C. 4"-Square size wafer was diced with a diamond saw into 4 pieces. After cutting, the substrates were put into the magnetron sputtering machine. The-400-nm thick



(a)

(b)

(c)

Fig. 1. (Color online) Design of sensors made using thin-film technology (figures are reproduced from the sources indicated in the reference list). (a) Ceramic microelectromechanical system (CeraMEMS) microcircuit based on a thin film of aluminum oxide (1) a ceramic substrate 0.6 mm thick with holes; (2) a layer of glass binder; (3) a thin film of aluminum oxide produced by electrolysis by spark oxidation of aluminum; (4) gas-sensitive layer; (5) laser-drilled hole; (6) platinum heater in the form of a meander; (7) contact pads to the heater and digit electrode; and (8) digit electrode to the sensitive layer.[19] (b) Schematic diagram of heating element after laser processing.[20] (c) Diagram (with dimensions) of a sensor structure based on MEMS technology.[17]

platinum layer was deposited on the glass substrate without a shadow mask. The 10 W YAG:Nd laser with a high-precision computer numerical control system was used for the engraving of the platinum heater. As a result, the dimensions of the hot part are about 500 × 500 μm^2, the thickness of the glass chip is of 30 μm, and the line width is equal to 60 μm.

Nanocrystalline undoped n-ZnO thin film is presented in Fig. 1(c).[17] This thin film was deposited on SiO_2/p-Si substrates (1–5 Ω cm, 5 × 5 mm^2) by a low-cost chemical deposition technique.

The most widely used membranes are based on aluminum oxide, and multilayer membranes are based on silicon with a platinum heater.[21,22] The advantage of aluminum oxide is that its coefficient of thermal expansion (CTE) is almost equal to the platinum CTE. Besides, platinum is characterized by sufficient adhesion to aluminum oxide since aluminum oxide is a strong material. However, the production of aluminum oxide membranes is a difficult process.[19,23]

Silicon technology is more mature and the production of membranes based on silicon oxide or nitride is easy. However, to equalize platinum and membrane CTEs and reduce thermal

stresses, it is necessary to produce multilayer membranes (SiO_2/Si_3N_4 in particular).[17] This will solve the CTE problem, but the problem of platinum adhesion still remains. Huang *et al.* tried to solve the CTE problem through the development of titanium interlayers and to improve the membrane stability at operation temperatures.[24] The heater itself can be spread on the membrane by vacuum deposition, screen printing or with a printer.[25–27]

Recently, articles on more unusual membrane materials such as ZrO_2/Y_2O_3 and borosilicate glass have been published; however, the softening temperature of the latter is below 600 °C.[20,28]

In the past decades, a large number of different semiconductor sensors have been developed to monitor hydrocarbons in the air. Nevertheless, there are different directions of development (sensor design, base and sensitive-layer materials, heating methods, and sensitive element spreading), including sensors to detect methane,[9,10,15–17] ethanol,[11,12,29,30] propane,[11,31] formaldehyde,[13] and other chemicals. The analysis results are shown in Table 2 with a brief description of the technology for producing a semiconductive SE, including operation temperatures and sensor sensitivity (S).

Table 2
Analysis results of research works.

Gas	SE	Membrane production technology	Operation temperature (°C)	Sensitiveness S[a] when exposed to 25 ppm of detected gas	Reference
C_2H_5OH C_3H_6O C_3H_8	In_2O_3–Ga_2O_3[b]	Production of targets of the composition 50% In_2O_3–50% Ga_2O_3, laser spraying	386–742	21,5 25,4 2,8	(11)
CH_2O	SnO_2 doped with Ga[c]	Spray pyrolysis	230	47,9	(13)
C_2H_5OH	WO_3–Ga_2O_3[d]	Thermal evaporation	200	0,65	(29)
H_2 C_3H_8	SnO_2/Pt/Pd[e] In_2O_3/AlO_3/Pt[e]	Sol–gel process	450 – 500	0,4 0,84	(31)
CH_3OH CH_4	$SnO_2/La_2O_3/MoO_3$/Pt[f]	Deposition of SnO_2 from the solution of $SnCl_4{\cdot}5H_2O$	415	146 50	(32)
CH_3OH CH_4	$SnO_2/La_2O_3/Va_2O_5$/Pt[f]			109 2,5	

[a]In the literature, the sensitivity S of semiconductor gas sensors is determined from the ratio $S = R_0/R_g$, where R_0 and R_g are the membrane resistance in the atmospheric air and in the air with the breakdown of the detected gas.

[b]Firstly the production of targets of the composition 50%In_2O_3–50%Ga_2O_3 from indium and gallium oxide powders was carried out. Secondly pulsed laser spraying of these films from the obtained target onto substrates made of sitall was carried out.

[c]The facile hydrothermal method was used. The presence of Ga in the SPMs and their structure were determined by X-ray powder diffraction (XR), energy-dispersive spectroscopy (EDS), X-ray photoelectric spectroscopy (XPS), and scanning electron microscopy (SEM).

[d]Ga_2O_3–core/WO_3–shell nanostructures were synthesized by thermal evaporation of Ga_2S_3 powders followed by thermal evaporation of WO_3 powders.[29]

[e]The measurements were carried out using sensors on a substrate of nanostructured aluminum oxide with different sensitive layers: SnO_2 + Pt + Pd for the first sensor. In_2O_3 + Al_2O_3 + Pt for the second. Because of the structural porosity of the formed materials, their specific surface area is about 30 m^2/g. A resistive layer is a heater made of inert materials (Pl, RuO_2, Au, etc.) and electrically isolated from the semiconductor layer.

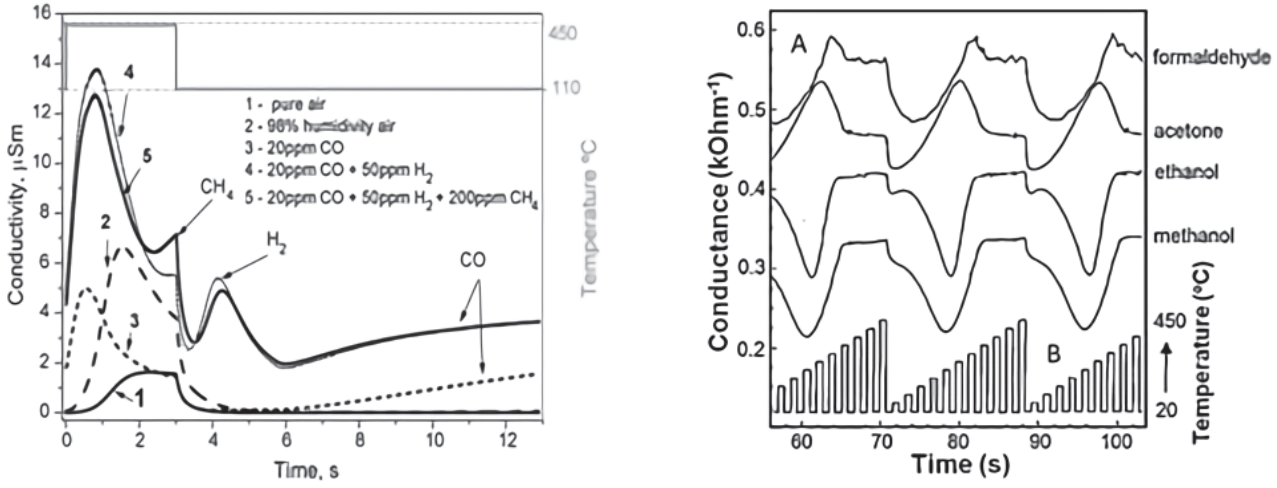
[f]Hydrothermal synthesis was used. The deposition of the material was carried out from a solution of $SnCl_4{\cdot}5H_2O$ and the corresponding alloying additives (namely, 4% $LaCl_3$*$7H_2O$; in the case of vanadium, the salt Na_3VO_4*$12H_2O$ was used; and with molybdenum, Na_2MoO_4*$2H_2O$) with an ammonia solution.

As for the methods of measuring, the main trend is the development of impulse and dynamic modes during which the temperature of a sensitive element changes.[11,19,33,34] During heating the volume of received data increases, which improves the measurement selectivity (Fig. 2) while maintaining high sensitivity. Therefore, it is possible to develop effective multisensory monitoring systems with milliwatt energy consumption.[16]

Passive or active filters are placed over sensitive materials to improve the selectivity of the sensor.[36,37] The passive filter is used extensively for different commercial sensors to absorb interfering gases, such as VOC. Since the passive filter relies on physical adsorption, the filter tends to be saturated with continuous exposure to VOCs. Compared with the passive filter, the active filter can reduce the size and cost of the device.

A novel on-chip microfilter was designed for MOS gas sensors.[38] The on-chip microfilter is fabricated from porous alumina ceramics loaded with platinum on the surface. The active filter was continuously heated by sensor chips. It was shown that both selective and sensitive responses to methane were enhanced by the on-chip microfilter. The sensor shows high sensitivity to CH_4, but has a high cross sensitivity to CO and VOC. Additionally, it was shown that the on-chip microfilter was not only limited to tin dioxide, but also valid for indium-oxide-based sensors.[39] However, the use of filters does not solve the problem of selectivity for gases from the methane homologue row.

On the basis of the analysis, we can conclude that although semiconductor sensors can be used for hydrocarbon monitoring in the range of pre-explosive concentrations, their main purpose is to monitor the impurities in the air in industrial and residential areas within the ppm concentration range.



(a) (b)

Fig. 2. (Color online) Sensor response in various operating modes: (a) response of a sensor operating in a cyclic pulsed heating mode (heating up to 450 °C for 3 s with subsequent holding at 110 °C for 10 s) to methane, carbon monoxide, and hydrogen;[15] (b) response of a sensor based on a Pd-doped SnO_2 film to saturated vapors of acetone, formaldehyde, ethanol, and methanol at 20 °C in the schematically illustrated repeating temperature sequence (the temperature pulse sequence actually was much denser in time: a sequence of temperature pulses consisting of 100 ms pulses in the range from 20 to 450 °C with a temperature step of 5 °C).[35]

3. Optical Sensors

The main advantage of optical technology is the noncontact analysis of detected gas concentration.[40] The nondispersive infrared method is the main technology used in infrared gas sensors. The technology is based on the ability of detected gas molecules to absorb infrared radiation. The change in the detected gas concentration in the air causes the change in the IR-ray absorption.

Apart from the widely used adsorption method of gas composition spectrum analysis, there are other principles of optical sensor operation.[41] In particular, it is possible to record the change in the spectra of diffuse dispersion or light reflection from the base layer or the change in luminescence intensity of an SE containing organic luminophores (their change depends on the interaction with the molecules of the detected mixture).

The main parts of an optical sensor are the radiation source and receiver, operating chamber, selective reflector, and processing and connecting board.[42] The optical scheme of optical sensors is traditionally based on a two-channel measurement scheme with the use of operation (measuring) and reference (comparative) channels. The operation channel uses a wavelength of light that is absorbed by the hydrocarbon, in particular, methane, and the reference channel uses a wavelength that is not absorbed, but which is close to the absorbed wavelength in order to exclude the influence of uncontrolled factors. In this case, two options for the implementation of optical measurements are possible: in an open space where the light source and receiver are located at a considerable distance from each other (Fig. 3) and in an enclosed space where the light source and receiver are integrated into the optical sensor case (Fig. 4). In the first case of the open path gas analyzer, it is possible to determine the presence of hydrocarbon in the space between the radiation source and receiver, but it is impossible to determine its concentration since the length of the path on which absorption occurs is unknown. In the second case, the concentration of combustible gas at the location of the optical sensor is measured. Thus, with the help of infrared (IR) spectroscopy, it is possible to carry out both remote measurements of

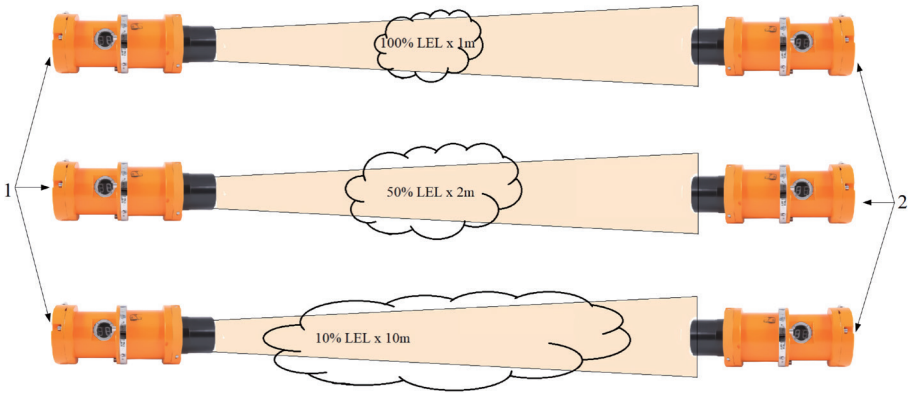


Fig. 3. (Color online) Principle of measurement using open path gas analyzer: (1) light source and (2) emission receiver.

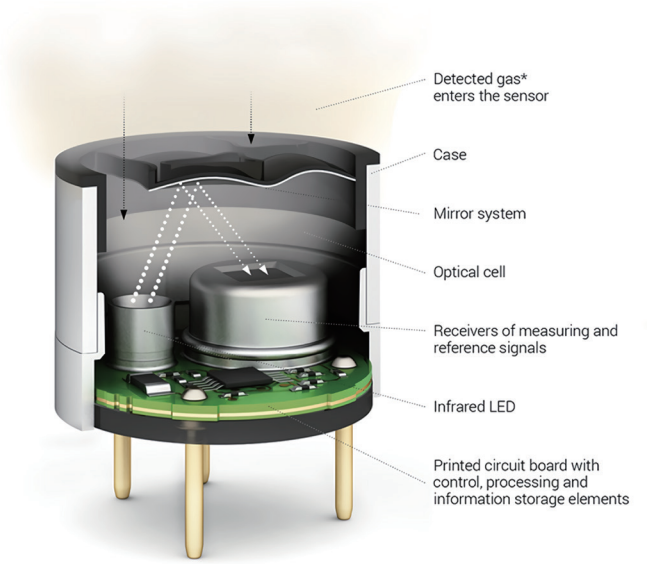


Fig. 4. (Color online) Optical sensor for local measurements.[43]

combustible gases along extended objects (for example, along the perimeter of enterprises) and local measurements (at the location of the optical sensor).

The optical sensor operation is based on the recording of a change in radiation intensity interacting with the examined gas environment at some wavelengths typical of this environment. To identify the wavelength operation and range from the radiator's broadband spectrum, interfering filters and discrete radiation are used at one or several wavelengths.[44,45]

The advantages of optical sensors include high sensitivity, selectivity, resistance to poisoning, fast response to the concentration increase, and the ability to operate in an anoxic environment. Their disadvantages include the inability to identify gases that do not absorb infrared rays (such as hydrogen); increased maintenance cost in difficult environments of use and, as a result, increased sensor cost.

The main advantage of optical sensors, compared with other sensors, is the absence of the direct contact of the detected mixture with the radiation source and receiver since the ray of light passes through the gas environment and the source and receiver are protected by transparent windows made of chemically resistant glass. Therefore, optical sensors are resistant to aggressive chemicals and compounds that incapacitate other types of sensor based on chemical reactions. Besides, optical sensors can be adjusted for other gas types by changing the radiation wavelength.

Optical sensors can operate in a wide temperature range (from −60 to +85 °C) and can be used both in closed and open spaces and in places where methane, propane, or oil product vapors arise, including anoxic environments.

Recently, many systems of hydrocarbon detection in the air have been discovered on the basis of infrared absorption spectroscopy.[46,47] The most promising direction in the development of gas analysis systems to control pre-explosive concentrations of flammable gases and flammable liquid vapors is now an optical-absorption method in the wavelength range of 3000–4000 nm, as this range includes the absorption lines of most hydrocarbons (Fig. 5).[48]

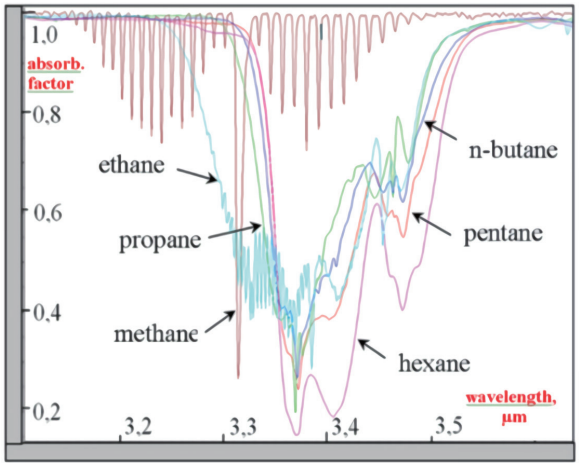


Fig. 5. (Color online) Experimental absorption spectra of hydrocarbons (methane CH_4, ethane C_2H_6, propane C_3H_8, butane C_4H_{10}, pentane C_5H_{12}, and hexane C_6H_{14}).[48]

Most research studies on optical sensors are on methane sensors. In the near-IR region, the methane spectrum has three absorption lengths at the wavelengths of 1.65, 2.33, and 3.3 μm. Methane LEL is 4.4%. In this case, the monitoring task is to detect methane at approximately 1%.

Until recently, the analysis of methane concentration in the air has been based on the most absorbing methane line at the wavelengths of 3.3–3.4 μm. In this case, miniature filament lamps were used as sources of radiation (including xenon ones) with a continuous spectrum in the near-IR region. As xenon lamps emit radiation in a wide wavelength spectrum, interference filters should be used as a compulsory measurement condition.

Currently, we can see the possibilities of producing semiconductive light-emitting diodes (LEDs), laser diodes, or adjustable distributed-feedback (DFB) lasers radiating at almost any wavelength in the near-IR region (1.6–5.0 μm) owing to the breakthrough in the technology of semiconductive heterostructure production.[45] This technology improves optical sensor parameters (size, energy consumption, and reliability) significantly. In particular, it has resulted in the development of methane gas analyzers at the wavelength of 1.65 μm.[49] However, the 1.65 μm methane line is weaker than the 3.3 μm line and lies closer to the strong line of water absorption. This complicates the analysis when using semiconductive LEDs as light sources because their radiation band is quite broad. Therefore, adjusted laser diodes with radiation at the wavelength of 1.65 μm, such as DFB lasers, are used as radiation sources.[50] Since the methane spectrum is lined and the laser diode line is very narrow, it is necessary to configure it to one of the absorbing bands when using this method and to stay within it independently of the environment conditions, semiconductor temperature, and current in the laser structure. In general, lasers with adjustable frequency are more expensive and difficult to operate than LEDs.

Note that the use of semiconductor light-emitting structures at the wavelength of 3.3 μm is complicated because of the narrow width of the banned area equal to approximately 0.38 eV. Therefore, at the temperature above 20 °C, there is the transition to intrinsic conductivity, which reduces the radiative recombination and, accordingly, requires either forced cooling to a

temperature below the normal one or a complex electrical scheme of power supply control and special algorithms of signal processing.[51,52] Moreover, the optical power of the near-IR-region LEDs (0.8–2.5 μm) is incomparably greater than that of the average IR region (2.5–25 μm).

The problems mentioned above can be partially solved by the development of an explosive gas optical sensor with ultralow energy consumption based on heterogenic semiconductive structures.[52] The energy consumption of this sensor is the lowest, i.e., under 5 mW.

Sensors with other measurement principles are also being developed. Dorozinsky *et al.* studied the possibility of surface plasmon resonance usage to detect methanol vapors.[53] Surface plasmon resonance is a violation of the full inside reflection condition under which a significant part of light energy reaching the metal film surface is converted into the energy of plasmons; as a result, the light intensity reflected from the surface of a metal film sharply decreases.[54] Experimental research proved the possibility of using such a decrease in accordance with the maximum permissible concentration requirements (5 mg/m^3, which approximately equals 0.37%); an almost linear dependence was established in the range of methane concentration in air from 0.05 to 1 vol.%.

Infrared spectroscopy can be used both in local (at the optical sensor location) and distant gas measurements along contiguous areas (for example, along the perimeter of a plant, pipelines, etc.). Open-path detectors may be used for the latter.[55–57]

The open-path detector consists of two separate block—radiational and measuring—which are placed at a distance from one another (Fig. 3). Halogen lamps or semiconductive structures based on GaInAsSb/AlGaAsSb (in the wavelength range of 1.6–2.4 μm) and InAsSb/InAsSbP (in the wavelength range of 2.7–4.7 μm) can be used as radiation sources and receivers.[57] Various authors have presented an optical scheme based on two beams with wavelengths of 2.3 and 1.7 μm.[55–57]

Recently, fiber optic gas detectors have been developed.[58] Their operation is based on the interferometric or absorption measurement method. The introduction of a special optic fiber and the optimization of different parameters improve the detection features. However, these methods require expensive equipment and a complex method of data processing and analysis. In this case, the optic fiber carries the light to the measurement point (to optical detectors). The gas arising in any of the detectors partially absorbs the light and generates a unique and concentration-dependent feature in the reflected signal. The analysis of reflected signals reveals the gas concentration at each monitoring point.

The sensitivity and resolution of the absorption spectroscopy technique are seriously affected by different types of noise (intrinsic laser noise, white noise, 1/f noise, and interference noise). Therefore, a highly precise and efficient processing of the measured spectra is crucial. Software-based filtering techniques have become a preferable choice because of their simplicity of implementation and low cost.

A novel methane sensor based on a direct absorption spectroscopy technique with a neural network filter was proposed and experimentally demonstrated.[59] The scarce data problem was overcome by using simulated absorption spectra that are highly consistent with practical experimental conditions to construct and train the neural network filter. The proposed neural network filter showed the best performance compared with several widely used filtering algorithms.[60,61]

Many different detection techniques have been applied to combustible gas detection, such as Fourier transform infrared spectroscopy, cavity-enhanced absorption spectroscopy, photoacoustic spectroscopy, and quartz-enhanced photoacoustic spectroscopy. However, owing to the effects of temperature, humidity, vibration, and noise, these technologies, except adsorption spectroscopy, are difficult to adapt to full-range detection and hazardous site applications, such as coal mines, natural gas pipelines, and chemical enterprises.

On the basis of the optical sensor analysis, we can conclude that optical sensors are under active development.[41] The main trend is the shift from lamp radiation sources to semiconductors as well as the development of fiber optic gas analyzers and open-path detectors. As the technology advances, the sizes of radiators and detectors are being reduced, which makes miniaturization one of the main directions of such device development.

4. Catalytic Sensors

A catalytic sensor is a heater with a porous oxide carrier on it (Al_2O_3 is mainly used) saturated with a catalyst containing platinum group metals. The operating principle of the catalytic sensor is to increase the heater temperature using the warmth emitted during the flameless hydrocarbon burning in the catalyst. The increase in the temperature causes the change in the electrical resistance of the heater with an almost linear dependence on the gas concentration. Moreover, the electrical resistance change in the corresponding measurement scheme is transformed into an output signal. An almost linear output characteristic in the range of the pre-explosive flammable gas concentration is the benefit of catalytic sensors.

Owing to the catalytic oxidation of flammable gases, catalytic sensors respond to almost all flammable gases and vapors, which creates opportunities to determine the leakage of any flammable gas mixture regardless of its composition.

Alongside that, the main drawbacks of these sensors are low selectivity to certain flammable gases, which causes a false response from inappropriate flammable gases and vapors (such as vapors of alcohol, paints, and varnishes), and high energy consumption (around 100 mW) preventing the production of devices capable of long-term service. In addition, their sensitivity is reduced by 10% or more per year of operation, which causes the need to check and change them regularly. Sensors can undergo poisoning by different gases that can be produced during industrial or household use as well as burnout. Both factors cause operability loss.

To improve the operation characteristics of catalytic sensors and overcome the disadvantages mentioned above, it is necessary to carry out research and development directed at the production of energy-efficient and highly sensitive selective catalytic sensors and measurement methods of flammable and explosive gases and their mixture concentration, including those with unknown composition, as well as the methods of their protection from operability loss.

A typical catalytic sensor consists of two sensitive elements (operational and comparative) included in a bridge scheme, that partially compensate for the change in environmental parameters. The difference between the operational and comparative elements is that a catalyst is applied on the operational element. The comparative element is not sensitive to flammable gases and is designed to compensate environmental parameters.

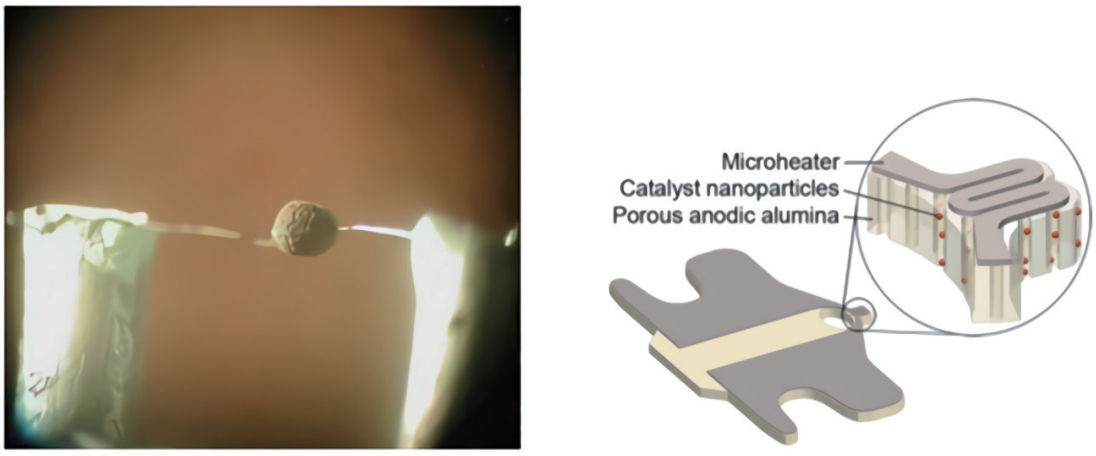
Catalytic sensors are specialized in flammable gases such as methane, propane, and hydrogen, and flammable liquid vapors such as benzol, toluene, and acetone.[62–67] Catalysts containing platinum group metals are the most widely used and promising for use in catalytic sensors owing to their high activity at 400–500 °C, which corresponds to the temperature range in which the use of platinum heaters is possible both as freely suspended helixes (pellistor-type catalytic sensors) [Fig. 6(a)] and as meanders [Fig. 6(b)] spread on the base layer (or membrane) using thick- or thin-film technology.[19,68–70]

Roslyakov *et al.* proposed to use a membrane made of porous anodic aluminum oxide films (AAO), on which a platinum microheater is applied.[68] To ensure catalytic activity, bimetallic Pd–Pt catalytic nanoparticles were successfully embedded inside AAO channels. This result demonstrated the applicability of micro-hotplate catalytic sensors based on porous anodic alumina supports for methane detection. The sensor sensitivity now approaches the value of 15 mV/vol.% for CH_4.Palladium or both palladium and platinum are the most widely used platinum group metals. In this case, catalysts with both palladium and platinum are more active.[72,73]

To register the response of catalytic sensors, both a bridge electric scheme and a scheme with a divisor are used.[74] The necessity of compensating for environmental parameters (temperature, humidity, and pressure) in the scheme with a divisor is compensated by using different signals at the two different temperature points.[75]

Direct current voltage (or periodically repeated impulses), alternating current voltage, multistage heating impulses, and temperature scanning are used as heating sources.[15,76–79] To form multistage voltage impulses, pulse width modulation (PWM) is often used, and linear voltage stabilizers are used for direct current voltage.[8]

One of the most frequent reasons for catalytic sensor breakage is the platinum helix burnout. As the temperature of the sensor is more or less stable, the bridge measurement scheme leads to sensor burnout to a lesser extent. The main way to protect the heater from burnout is gradual sensor heating. During this process, heating takes more time, which leads to an increase in the



(a) (b)

Fig. 6. (Color online) Appearance of catalytic sensors of different types. (a) appearance of the pellistor type of catalytic sensor, hung on the metal pillars of the case[71] and (b) 3D model of a planar sensor type.[68]

consumed power. The use of pulse-duration modulation should ensure a relatively low speed of heating with increased catalytic sensor breakage resistance while preserving low power consumption.

As a rule, each catalytic sensor is calibrated to a certain gas (methane, propane, and other hydrocarbons). However, at petrochemical plants, there are mixtures of explosive hydrocarbon gases and vapors with unknown compositions in the air. Therefore, there is an urgent need to define the explosiveness of flammable gas mixtures and vapors when the composition and concentrations of the components are unknown. The solution will make it possible to expand the range of technical means to warn against and prevent emergencies related to the leakage of flammable gases in petrochemical plants and residential areas.

To conduct measurements, a catalytic sensor is calibrated at two points: at zero and a predetermined gas concentration (in the range of LEL concentrations of flammable gases, the sensor response is linear). Thus, as a matter of fact, the sensor end temperature is measured at a known concentration; therefore, the result is only one measured temperature value (the value of voltage or current in accordance with the scheme solution). The sensors are usually calibrated to methane; there are conversion coefficients for measuring the other hydrocarbon concentrations. To use them, the hydrocarbon type in the air should be known.

Therefore, if there is a task to measure the concentration of gas mixture components, multisensory gas detectors, optical spectrometers, or other multigas analyzing equipment are required.[80,81] This certainly adds complexity to the equipment and methods of conducting measurements as well as extends and increases the monitoring process costs.

The evaluation of the flammable gas mixture explosiveness starts with the detection of all the gases in the mixture. Then, the concentration is determined, and the gas mixture LEL is measured and compared with the theoretical value for this mixture. On the basis of results of the comparison, the level of explosiveness is evaluated. At the same time, the detection of flammable gases in the mixture to determine the explosion probability is a necessary subtask to determine the gas mixture LEL in the conventional approach. Therefore, this is a promising approach to determine the level of explosiveness of hydrocarbon gases and vapor mixtures without precise gas detection.

Recently, for this purpose, a method has been developed for determining the explosiveness level of multicomponent hydrocarbon gas mixtures with unknown gas compositions. The method is based on measuring the thermal effect during burning of a hydrocarbon mixture inside the catalytic sensor.[82]

The proposed method of determining the explosiveness level of multicomponent hydrocarbon gas mixtures with unknown gas composition is based on the fact that the product of a certain gas LEL value and heat burning value (Q_0) is approximately the same for most flammable gases and vapors (±10%) (Table 3). Therefore, if the heat emitted during burning in the sensor chamber is measured, it is possible to determine the probability of a flammable gas mixture explosion without knowing its composition (whether it is a mixture of gases or a certain gas).

The amount of heat emitted is determined through the measurement of the sensor response during heating to the operation temperature both in the absence and presence of flammable

Table 3
Analysis results of research works.

No.	Flammable gas	Concentration C_{LEL}, %vol., RU/US + EU	Standard combustion heat Q_0, kcal/mole	$C_{LEL} \times Q_0$, kcal/mole, RU/US + EU
1	Methane CH_4	4.4/5.0	191.554	8.428/9.77
	Ethane C_2H_6	2.5/3.0	344.3	9.411/10.34
	Propane C_3H_8	1.7/2.1	498.6	8.49/10.47
	Butane C_4H_{10}	1.4/1.6	661.1	9.25/10.57
2	Benzene C_6H_6	1.2/1.3	832.88	9.99/10.82
	Toluene C_7H_8	1.1/1.2	899.86	9.90/10.79
3	Methanol CH_3OM	5.5/6.7	182.43	10.034/12.22
	Ethanol C_2H_5OM	3.1/3.3	336.295	10.425/11.09
4	Ethylene C_2H_4	2.7/2.7	314.799	8.48/8.48
	Propylene C_3H_9	2.0/2.4	458.345	9.16/11.00
	Butane C_4H_8	1.6/1.6	607.29	9.71/9.71
5	Acetone $CM_3–CO–CM_3$	2.5/2.6	435.029	10.876/11.31
6	Acetylene C_2H_2	2.5/2.5	310.739	7.77/7.77

gases. The amount of heat emitted during hydrocarbon burning is determined as the difference in sensor response integrals from the time of sensitive element heating in the presence or absence of flammable gases. Thus, the measurement result is not one resistance value but the dependence of resistance change on the hydrocarbon burning time. This increases the amount of experimental data and enables the determination of the explosiveness of flammable mixtures with unknown compositions.

Advanced data processing is required to calculate the heat release. The processing is based on integrating the area under the measured dependence of the sensor response on time. Real-time integration of the sensor response, which is calculated during a two-stage heating pulse, simplifies data processing.[83]

The experiments were carried out for various mixtures of methane, propane, butane, and hexane within the pre-explosive range (up to 50% LEL).[84] Mixtures of two or three different components were evaluated with the prescribed mixture concentration in LEL units (C_{LEL}). To calculate the LEL of a mixture of flammable gases, Le Chatelier's rule[85] was used. The measurement LEL values correlate with the prescribed C_{LEL} values. Since in this approach, there is no need to identify gases, their quantity or component concentrations, it can be used in industry for the quick determination of potentially explosive mixtures in the air.

Various authors proposed the method of manufacturing catalytic sensors where stabilized platinum nanoparticles are used as a catalytic layer.[64,66] Their results showed that the response time is short, <150 ms. Furthermore, direct contact with the detector and a high Seebeck coefficient resulted in a high resolution and sensitivity of 0.22 mV/10 ppm with a significantly reduced energy consumption.

Lashkov *et al.* described the realization of a catalytic sensor that includes an Al_2O_3 sensitive layer loaded with Pd and Pt by utilizing a solution of $PdCl_2$ and H_2PtCl_6.[67] Their test showed that it is possible to produce catalytic chips providing a signal for the detection of gas mixtures of the same type. The main disadvantage is the absence of thermal insulation between the silicon crystal and the chip body as well as between the adjacent sensor elements. The reduced need to

eliminate heat may lead to a decrease in chip energy consumption and to a stability increase of sensor values over time.

Somov *et al.* described a method of modifying the catalytic sensor measurement circuit to detect gas concentrations from 100 ppm to 100 vol.% instead of the typically applicable range of 0.1–10 vol.%.[86] The extension of the detection range is enabled by using two sensors with catalysts in the modified Wheatstone sensing circuit and covering them with sealed caps with different holes to enable gas diffusion control.

Catalytic sensors are exposed to poisoning by different components such as organosilicon, organophosphorus, sulfur, and other compounds that may be contained in the atmosphere of oil and gas plants as well as residential areas. Such poisoning leads to sensor sensitivity reduction and, as a result, operability loss. This catalyst poisoning is irreversible as even small concentrations of poisonous chemicals in the gas–air mixture degrade the parameters of the catalytic sensor over time. To prevent poisoning and increase the catalytic sensor durability, corresponding filters will be developed to pass gases while entrapping poisoning gases.[87]

Despite the fact that catalytic sensors have been developed for more than 50 years, they have not yet been perfected. Their main advantages are linear (although different) sensitivity to all hydrocarbons and relative simplicity of construction. The main issue is the instability of sensitivity, which changes over time and depends on environmental factors (mainly humidity and catalytic poisons), as well as a low selectivity. Contemporary studies are being conducted to solve this problem.

Samotaev *et al.* developed a reduced catalytic gas sensor for the detection of methane.[88] The sensor chip is formed from two membranes with a 150-μm-diameter heated cover with a highly dispersed nanosized operational element and an inert comparative element. The sensitivity of the device is 10 mV/%, and the response and recovery times are <500 ms and <2 s, respectively. However, the high degradation rate of the catalyst coupled with its modest chemical power limits the use of the sensor to pulsed-mode operation.

To improve the parameters of catalytic sensors, mathematical methods for processing the obtained data are increasingly being used. The application of mathematical methods requires an increase in the amount of experimental data. Therefore, a promising approach seems to be associated with processing the results of not just the response value at a given sensor temperature, but also the dependence of the catalytic sensor response on the applied voltage (U) $N = f(U)$ (which is equivalent to a change in temperature).

A novel temperature modulation method for enhancing catalytic sensor selectivity was proposed and applied to the detection of methane and saturated vapors of acetone, ethanol, and gasoline.[89] The data were treated by machine learning methods. As a result, it was possible to recognize different combustible gases and vapors in a mixture using a single catalytic sensor.

In addition, the principal component method (PCA) and linear discriminant analysis (LDA) can be used to analyze the dependence $S = f(U)$.[90,91] Such mathematical processing makes it possible to separate combustible gases in multicomponent gas mixtures.

(a) (b)

Fig. 7. (Color online) Sensors with built-in control board and digital output: (a) miniature wireless sensor[92] and (b) intelligent sensor module manufactured by Inkram.[93]

5. Conclusion

The development of sensors of flammable gases and VOCs at pre-explosive concentrations needs to meet constantly increasing requirements for industrial, household, and ecological safety. At the same time, most research works on MOS, optical, and catalytic sensors are devoted to methane detection for the following reasons.

(1) In terms of industrial safety, the interest in methane sensors is caused by the increase in the production, transport, storage, processing, and use of methane as a fuel.
(2) In terms of ecological safety, the interest in methane detection is fueled by the increase in atmospheric pollution not only near refineries and chemical plants but also in residential areas. In addition, methane is a by-product of agriculture. Moreover, methane is a greenhouse gas that retains atmospheric heat.
(3) In terms of household safety, the interest in methane monitoring is related to, first of all, the necessity to prevent explosion hazards caused by methane leakages in residences with a gas supply.

It is clear that sensors with different features and parameters, as well as low cost, are required for industrial, ecological, and household safety. Therefore, all flammable gas sensors reviewed here will continue to broaden their range of use. However, outside for conventional parameters such as sensitivity, selectivity, and parameter stability in different environments, new requirements are also imposed on sensors because of the contemporary development of electronics, wireless data transmission, power supply sources, and energy accumulation systems.

The miniaturization of electronic components and circuit board technology allows one to insert boards in the sensor body, digitalize, process, and correct the analog sensor signal, and analyze the results on the spot (Fig. 7).[92,93] As a result, more complex algorithms of measurement can be used to receive and process more data, thereby improving selectivity, sensitivity, and measurement accuracy. At the same time, special attention is being paid to the use of neural networks and machine learning methods.

The development of energy-efficient wireless technologies (Zigbee, Bluetooth, NFC, etc.) is the way to stop using cable data transmission lines. This is a trend that is occurring in many fields in the world, and sensor technology is not an exception.

The development of accumulators and batteries together with energy consumption reduction in the sensors themselves and in the electronic component base will promote the production of gas analyzers capable of working autonomously for over one year.[6] The application of solar, heat, microwave, and wind energy collection and accumulation will make gas analyzers fully independent of power supply lines.[94,95] In this case, if the sensor operates autonomously for a long time, the requirements for the long-term stability of its parameters will become stricter since one must be sure that there is no degradation of the sensor parameters.

On the basis of the above, the main development direction of sensors of flammable gases and VOC at pre-explosive concentrations is towards the creation of energy-efficient semiconductor and catalytic sensors produced using planar technology with a transition from optical sensors to semiconductor LEDs, laser diodes, and lasers with tunable wavelength, obtained using the technology of semiconductor heterostructures.

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